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WASTES INTO PRODUCTION

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BLACK CERAMIC PIGMENTS BASED ON OPEN-HEARTH SLAG

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Black ceramic pigments based on open-hearth slag are obtained. The possibility and sequence of physical-chemical processes occurring during kilning of pigment mixes are evaluated and the nature of the color-carrying phases in the products of their heat-treatment is determined. The relation between the crystal-phase composition and the optical indicators of the slag-containing pigments is studied. It is shown that such pigments are promising for coloring various glazes.

Key words: ceramic pigments, open-hearth slag, physical-chemical processes, color, crystal-phase composition, optical indicators, glazes.

As a rule, black ceramic pigments are made from commercially pure iron oxides, chromium, manganese, cobalt, nickel and copper taken in definite proportions, which has a negative effect on their cost of production. For this reason, it is desirable to expand the raw materials base by using unconventional (secondary) materials from various sectors of industry, specifically, the metallurgical sector, to produce pigments of this kind.

The present work studies the possibility of using open-hearth slags as the base raw material for the synthesis of black ceramic pigments.

Waste open-hearth slag from a metallurgical plant in Dnepropetrovsk was used in the present work. The slag was first magnetically enriched and blended.

The complex of physical-chemical studies (chemical, x-ray, and differential-thermal analysis) of the pigment part (fraction < 0.25 mm) of such open-hearth slag showed that it has a high content of iron compounds (total content by weight 24.33%) as well as Cr_2O_3 and MnO — 2.47 and 3.36 wt.%, respectively (Table 1). In addition, the iron is largely concentrated in magnesioferrite $MgFe_2O_4$ and magnesiowustite (so-called RO-phase). The principal silicate phase of the experimental slag is â-slag; comparatively small amounts of merwinite $3CaO \cdot MgO \cdot 2SiO_2$ and the products of its hydration — afwillite $3CaO \cdot 2SiO_2 \cdot 3H_2O$ — are also present. In addition, XPA shows that calcium carbonate $CaCO_3$ in the form of calcite, which is the result of an interaction between residual free lime and atmospheric air, was recorded in the experimental slag.

To obtain black ceramic pigments, chromium and cobalt oxides were additionally added in amounts to 30 wt.% for milling the initially obtained powder of the experimental waste obtained (fraction < 0.25 mm). Next, the mixes obtained were kilned in air in a laboratory electric furnace with

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TABLE 1. Data from Chemical Analysis of the Pigment Part of Open-Hearth Slag*

Sample designation	Component content, wt.%													
	SiO_2	Al_2O_3	Fe_{met}	Fe_2O_3	FeO	TiO_2	Cr_2O_3	CaO	MgO	MnO	ZnO	$K_2O + Na_2O$	Other	Sum
d	26.96	6.95	0.36	15.80	8.17	0.34	2.47	12.62	13.98	3.36	0.12	0.36	8.51	100

* The pigment part of the experimental slag was obtained by wet milling the initial sample in a ball mill for 5 h and then passing the product obtained through a No. 025 sieve and drying.

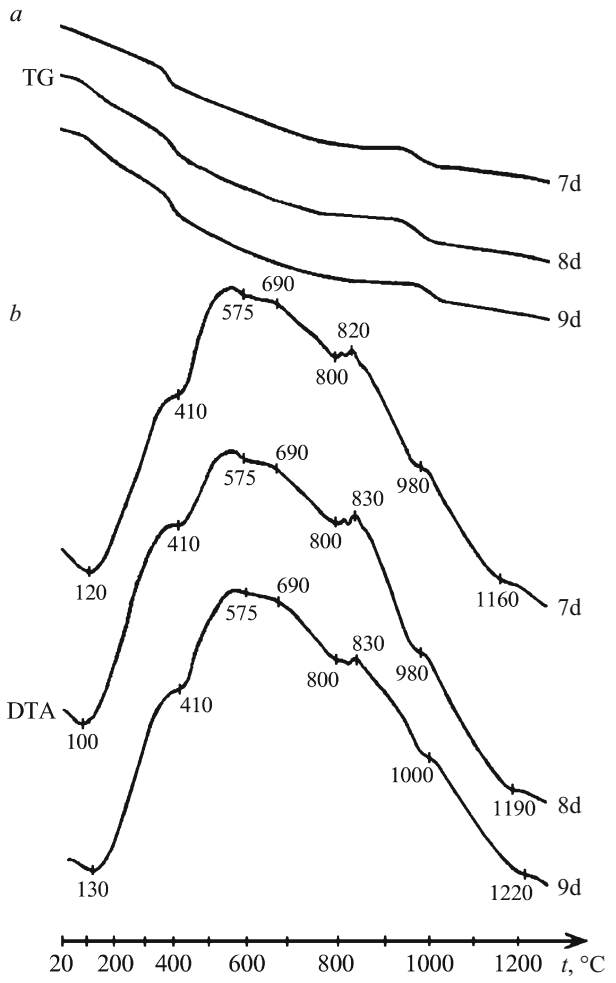

Fig. 1. Differential-thermal analysis of the experimental pigment mixes: *a*) thermogravimetric curves (TG); *b*) differential-thermal curves (DTA).

maximum temperature 1200 °C and isothermal soaking for 1 h.

It was established experimentally (Table 2) that the degree of sintering of the ceramic pigments synthesized in the system Dnepropetrovsk open-hearth slag – Cr_2O_3 – CoO increases as the cobalt oxide content in them increases (to 30%). Endo effects in the temperature interval 1160 – 1220 °C are observed in the DTA curves (Fig. 1). Since chromium oxide increases the refractoriness in the indicated system the corresponding endo effects shift to higher temperatures as its content in the raw materials mixes increases.

The character of the color change of the synthesized pigments shows an extremal dependence with the highest intensity of the black color for ratio $CoO/Cr_2O_3 = 2/1$, which is confirmed by the minimum value of the diffuse reflection coefficient 9.85%.

To evaluate the possibility and sequence of formation as well as to determine the nature of the color-carrying phases in the products of heat-treatment of the pigment mixes, we performed thermodynamic calculations of the change of the Gibbs free energy ΔG as a function of temperature for the principal chemical reactions, as well as differential-thermal and x-ray phase studies.

The thermodynamic constants presented in the reference literature [1 – 4] and summarized in Table 3 were used for the calculations. The missing coefficients in the equation for the heat capacity $C_p = f(T)$ were found by N. A. Landiya's method [5]. The change of the Gibbs energy was calculated using the well-known algorithm for silicate systems [1].

The reactions for which thermodynamic calculations were performed are presented below:

$$4(Mg_{0.5}, Fe_{0.5})O + 0.5O_2 = 2MgO + Fe_2O_3; \quad (1)^3$$

$$2MgO + Fe_2O_3 + 0.5CoO = (Mg_{0.5}, Co_{0.5})Fe_2O_4 + 1.5MgO; \quad (2)^3$$

$$4(Mg_{0.5}, Fe_{0.5})O + 0.5CoO + 0.5O_2 = (Mg_{0.5}, Co_{0.5})Fe_2O_4 + 1.5MgO; \quad (3)^3$$

$$MgO + Cr_2O_3 = MgCr_2O_4; \quad (4)$$

$$CoO + Cr_2O_3 = CoCr_2O_4; \quad (5)$$

$$Ca_3MgSi_2O_8 + 2SiO_2 = CaMgSi_2O_6 + 2(\beta\text{-}CaSiO_3); \quad (6)$$

$$Ca_3MgSi_2O_8 + 3SiO_2 + CoO = 2[Ca(Co_{0.5}, Mg_{0.5})Si_2O_6] + \beta\text{-}CaSiO_3. \quad (7)^3$$

The computational results are presented in Table 4, while the change of the Gibbs energy for the indicated reactions as a function of temperature is illustrated in Fig. 2.

[3] An equal molar ratio of magnesium, iron, and cobalt oxides in the composition of the corresponding solid solutions was used in the calculations.

TABLE 2. Characteristics of the Synthesized Ceramic Pigments

Composition no.	Coloring oxides introduced, wt.%		Visual evaluation of the color and degree of sintering of pigments	DRC,* %
	Cr_2O_3	CoO		
7d	–	30.0	Sinter, prone to comminution, black color with blue tinge	10.51
8d	10.0	20.0	Strongly aggregated back powder	9.85
9d	20.0	10.0	Aggregated brown-black powder with a green tinge	11.55

* Diffuse reflection coefficient of pigment powders, measured on a KTs-3 color comparator.

The thermodynamic calculations established that in the experimental system the initial phase of the open-hearth slag, participating in the formation of a solid solution between magnesium and cobalt ferrites, for kilning in air is directly magnesiowustite — reaction (3). Exothermal effects at 690°C are observed on the DTA curves of the pigment mixes (see Fig. 1). The formation of a ferrite solid solution is confirmed by the presence in the pigment 7d diffraction pattern (Fig. 3) of the principal reflections ($d \times 10^{-10} = 4.80$, 2.94, 2.51, 2.09, 1.60, and 1.47 m) due to the cobalt and magnesium ferrite as well as by the presence of only residual divalent cobalt oxide ($d \times 10^{-10} = 2.46$, 2.13, and 1.50 m).

The large drop of the absolute value of the Gibbs energy for the ferrite forming reaction at temperature 1273 K (see Table 4 and Fig. 2) is due to the partial loss of oxygen by the solid solution formed; it agrees with the data obtained by Yu. D. Tret'yakov [6] and is also confirmed by differential-thermal studies performed on pigment mixes. Specifically, endothermal effects with minima in the temperature interval 980 – 1000°C are present in the DTA curves and the corresponding mass losses are present on the TG curves (see Fig. 1).

In addition, according to the calculations, it possible for cobalt oxide to enter into the diopside structure, since the probability of such a reaction is much higher than for diopside itself (see Table 4 and Fig. 2, reactions (6) and (7)).

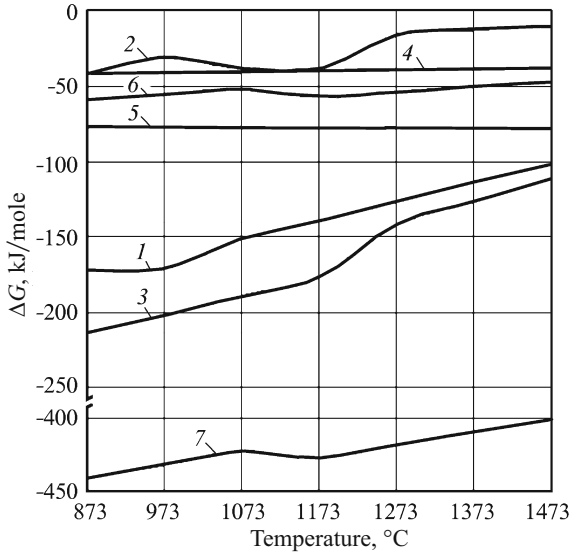

Fig. 2. Gibbs energy versus the temperature for the reactions (1) – (7).

TABLE 3. Initial Thermodynamic Constants of Individual Compounds

Compound	State*	$-\Delta H^0_{298.15}$, kJ/mole	$-\Delta G^0_{298.15}$, kJ/mole	$-\Delta S^0_{298.15}$, J/(mole · K)	$C_p = a + bT + cT^{-2}$, J/(mole · K)			Temperature interval, K
					a	$b \times 10^3$	$c \times 10^{-5}$	
MgO	Cr.	601.78	569.53	27.08	42.61	7.28	–6.19	298 – 2100
$(Mg_{0.5}, Fe_{0.5})O$**	Cr.	433.31	406.91	43.91	46.70	7.94	–4.75	298 – 1650
O_2	Gas.	0	0	205.04	31.46	3.39	–3.77	298 – 3000
α-Fe_2O_3	Cr.	823.80	740.69	90.00	98.33	77.86	–14.86	298 – 950
β–Fe_2O_3	Cr.				150.70	0	0	950 – 1050
γ–Fe_2O_3	Cr.				132.74	7.37	0	1050 – 1800
$MgFe_2O_4$	Cr.	1463.01	1353.42	129.77	190.04	0	0	665 – 1230
					107.45	56.85	0	1230 – 2000
$CoFe_2O_4$	Cr.	1087.94	980.65	134.79	145.94**	41.86**	0	783 – 1873
$(Mg_{0.5}, Co_{0.5})Fe_2O_4$**	Cr.	1275.47	1167.03	132.28	167.99	20.93	0	783 – 1230
					126.70	49.35	0	1230 – 1873
Cr_2O_3	Cr.	1141.10	1059.47	81.21	119.43	9.21	–15.66	298 – 1800
$MgCr_2O_4$	Cr.	1788.26	1673.71	106.07	167.52	14.90	–40.10	298 – 1800
CoO	Cr.	239.02	215.21	52.74	48.31	8.54	–1.67	298 – 2000
$CoCr_2O_4$	Cr.	1456.69	1351.24	133.95	167.65	17.74	–13.97	298 – 1800
$Ca_3MgSi_2O_8$	Cr.	4569.02	4340.23	253.25	305.45	50.06	–60.44	298 – 1605
α-quartz	Cr.	911.50	857.08	41.86	60.32	8.13	0	848 – 2000
α-tridimite	Cr.	905.98	852.19	43.53	57.10	11.05	0	390 – 2000
$CaMgSi_2O_6$	Cr.	3206.16	3032.02	143.09	221.21	32.80	–65.86	298 – 1600
β–$CaSiO_3$	Cr.	1636.52	1551.12	82.04	111.51	15.07	–27.29	298 – 1473

* State of material: Cr.) crystalline; Gas.) gaseous.

** Thermodynamic constants calculated by the present authors.

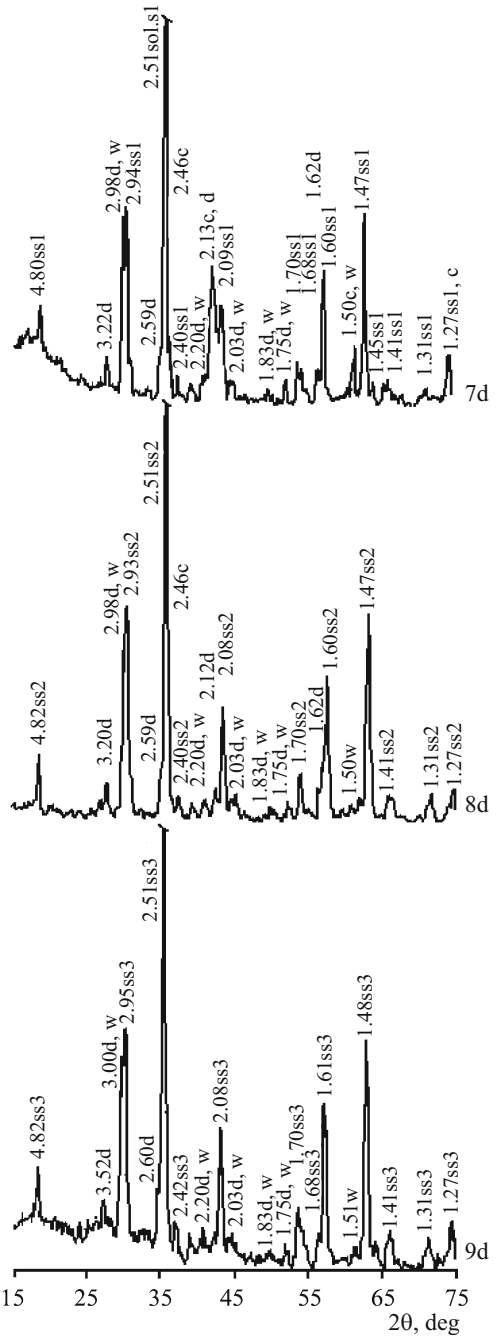

Fig. 3. X-ray diffraction patterns of ceramic pigments synthesized on the basis of open-hearth slag: ss1) solid solutions between $MgFe_2O_4$ and $CoFe_2O_4$; ss2) solid solution between $MgFe_2O_4$, $CoFe_2O_4$, and $CoCr_2O_4$; ss3) solid solution between $MgFe_2O_4$, $MgCr_2O_4$ and $CoFe_2O_4$, $CoCr_2O_4$; d) diopside; w) wollastonite; c) CoO.

The final reaction products in the experimental slag-containing pigments obtained by introducing chromium oxide together with a solid solution based on ferrites are likewise cobalt chromites $CoCr_2O_4$ and magnesium chromite $MgCr_2O_4$, which in view of the fact that the parameters of their crystal lattices with magnesium and cobalt ferrites are identical can form a single solid solution with variable composition. The formation of the indicated chromites agrees with x-ray phase studies (see Fig. 3), while it is precisely the reflections in the diffraction patterns at $d \times 10^{-10} = 4.82$, 2.95, 2.51, 2.08, 1.61 and 1.48 m that are seen while free chromium oxide is not. In addition, from the thermodynamic point of view, the formation of the cobalt chromite phase via the reaction (5) is energetically more favorable. The magnesium chromite can form (reaction (4)) when excess chromium oxide with respect to the stoichiometric spinel $CoCr_2O_4$ is present in the system, which to a large extent is characteristic for the fragment with composition 9d.

It follows on this basis that the main participants in the formation of color in the experimental slag-containing pigments are spinels ($MgFe_2O_4$, $MgCr_2O_4$, $CoFe_2O_4$ and $CoCr_2O_4$), which because of the closeness of their structure form solid substitution solutions. A rational relation between these spinels that is required to attain a black pigment obtains in the composition 8d. The shift of the quantitative ratio between them in the direction of increasing fraction of chromites is the reason for the manifestation of a green tinge (composition 9d), while an increase of the total content of cobalt oxide to 30 wt.% (composition 7d) gives a blue tinge.

To obtain colored glazes finely milled powders of the synthesized pigments were introduced into a transparent fritted glaze, intended for deposition on a facing tile, in the amount 8 wt.%. The glass coatings were kilned at the maximum temperature 1100°C and then rapidly cooled.

The color and optical properties of the glazes obtained are presented in Table 5.

It has been established experimentally that the most intense black color of a glass layer obtains by introducing ceramic pigment synthesized in the open-hearth slag – Cr_2O_3 – CoO system with coloring oxides ratio $CoO/Cr_2O_3 = 2/1$. This is confirmed by visual evaluation of the color of the glazes obtained and by the minimal value of the DRC (3.95%). Deviation of this ratio between the cobalt and chromium oxides in the experimental pigments results in other colors being dominant and, in consequence, the diffuse reflection coefficient increases from 5.14 to 5.66 %.

The black ceramic pigment developed in this work (composition 8d) was also successfully tested in a transparent nonfritted glaze for ceramic sanitary ware. The glass coatings so obtained were distinguished by high quality and low DRC (3.69%).

In summary, this investigation proved that it is possible to synthesize ceramic pigments in the system open-hearth slag – Cr_2O_3 – CoO. The regularities of the formation of the crystal-phase composition of such pigments and its relation with the diffuse reflection coefficient, characterizing the emissivity, were studied. The pigments developed make it possible to attain high aesthetic-decorative properties of the glass coatings with stable and intense black color.

TABLE 4. Computed Changes of the Gibbs Energy for the Reactions (1) – (7) in the Temperature Interval 873 – 1473 K

Reaction	Gibbs energy (kJ/mole) at temperature, K						
	873	973	1073	1173	1273	1373	1473
(1)	–172.5	–170.8	–151.3	–138.8	–126.2	–113.7	–101.2
(2)	–41.26	–30.7	–37.8	–38.0	–15.7	–12.6	–9.5
(3)	–213.8	–201.5	–189.1	–176.8	–141.9	–126.3	–110.7
(4)	–41.2	–40.6	–40.0	–39.4	–38.9	–38.3	–37.8
(5)	–77.2	–77.4	–77.5	–77.7	–77.9	–78.0	–78.2
(6)	–59.0	–55.4	–51.8	–56.9	–53.5	–50.1	–46.8
(7)	–440.0	–431.2	–422.4	–426.6	–417.9	–409.2	–400.7

TABLE 5. Characteristics of Glazes

Coating number*	Coating color (visual assessment)	DRC, %
7d	Intense blue-grey	5.66
8d	Black	3.95
9d	Intense dark-brown with greenish tinge	5.14

* This number corresponds to the pigment numbers in Table 2.

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